

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

| | | |
|--|---|--|
| Applicant's or agent's file reference P48544PC00 | FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. | |
| International application No. PCT/NL 00/ 00059 | International filing date (day/month/year) 28/01/2000 | (Earliest) Priority Date (day/month/year) 29/01/1999 |
| Applicant COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING et al | | |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

COMPOSITION BASED ON CROSS-LINKED STARCH AND DEPOLYMERIZED STARCH SUITABLE AS G ELATINE REPLACEMENT

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00059

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A23L1/0522 A23L1/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 5 576 043 A (STANKUS CAROL ET AL) 19 November 1996 (1996-11-19) column 3, line 16 -column 4, line 12 column 4, line 59 -column 5, line 58 examples 4,6; table I --- | 1-4,9, 12-15 |
| X | EP 0 768 042 A (NESTLE SA) 16 April 1997 (1997-04-16) page 2, line 48 - line 51 examples 1,2 --- | 1-3,9, 12,14 |
| X | EP 0 884 003 A (NESTLE SA) 16 December 1998 (1998-12-16) claim 1; example 1 --- | 1,3,9, 12,14 |
| | --- -/-- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

14 April 2000

Date of mailing of the international search report

26/04/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Vuillamy, V

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00059

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | US 4 504 509 A (BELL HARVEY ET AL) 12 March 1985 (1985-03-12) column 3, line 1 -column 4, line 51 table I | 1,2,9, 12,14 |
| X,P | EP 0 898 902 A (PENFORD CORP) 3 March 1999 (1999-03-03) page 4, line 4 - line 49 page 5, paragraph 2 tables 5-11 page 4 | 1-3,6,8, 9,12,14 |

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 00/00059

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| US 5576043 | A | 19-11-1996 | WO 9639863 A | 19-12-1996 |
| EP 0768042 | A | 16-04-1997 | AU 6814896 A | 17-04-1997 |
| | | | CA 2187807 A | 14-04-1997 |
| | | | CZ 9602971 A | 14-05-1997 |
| | | | JP 9107916 A | 28-04-1997 |
| | | | NZ 299542 A | 26-06-1998 |
| | | | PL 316472 A | 14-04-1997 |
| | | | SK 129496 A | 07-05-1997 |
| | | | US 5922391 A | 13-07-1999 |
| EP 0884003 | A | 16-12-1998 | AU 6995498 A | 17-12-1998 |
| | | | BR 9801807 A | 25-05-1999 |
| US 4504509 | A | 12-03-1985 | CA 1198624 A | 31-12-1985 |
| | | | JP 1274623 C | 31-07-1985 |
| | | | JP 59051749 A | 26-03-1984 |
| | | | JP 59051986 B | 17-12-1984 |
| EP 0898902 | A | 03-03-1999 | US 6022569 A | 08-02-2000 |
| | | | CA 2244935 A | 15-02-1999 |

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PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C.20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

| | |
|---|---|
| Date of mailing (day/month/year) 14 September 2000 (14.09.00) | |
| International application No. PCT/NL00/00059 | Applicant's or agent's file reference P48544PC00 |
| International filing date (day/month/year) 28 January 2000 (28.01.00) | Priority date (day/month/year) 29 January 1999 (29.01.99) |
| Applicant WOLTJES, Jakob, Roelf et al | |

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

11 July 2000 (11.07.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

| | |
|--|--|
| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35 | Authorized officer Olivia TEFY Telephone No.: (41-22) 338.83.38 |
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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

NRF 23-7-2001
NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

| | | | | |
|---|----------------------|---|--|--|
| nie jaar | TERMIJN | To: Mr Ir A.W. Prins, C.S. C/O VEREENIGDE Nieuwe Parklaan 97 NL-2587 BN The Hague | | Date of mailing (day/month/year) 06.02.2001 |
| | | PAYS-BAS 12 FEB. 2001 | | |
| | Beantwoord voorl. | bericht gezonden aan | | |
| | def. | Applicant's or agent's file reference | | |
| MAP | P48544PC00 | IMPORTANT NOTIFICATION | | |
| International application No. PCT/NL00/00059 | | International filing date (day/month/year) 28/01/2000 | | Priority date (day/month/year) 29/01/1999 |
| Applicant COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING et al | | | | |


1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

| | |
|--|--|
| Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 | Authorized officer Tantum, P Tel. +49 89 2399-8143 |
|--|--|




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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| | | | |
|---|---|---|--|
| Applicant's or agent's file reference P48544PC00 | | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) | |
| International application No. PCT/NL00/00059 | International filing date (day/month/year) 28/01/2000 | Priority date (day/month/year) 29/01/1999 | |
| International Patent Classification (IPC) or national classification and IPC A23L1/0522 | | | |
| Applicant COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING et al | | | |
| <p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p> | | | |
| <p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application | | | |
| Date of submission of the demand 11/07/2000 | | Date of completion of this report 06.02.2001 | |
| Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 eprmu d Fax: +49 89 2399 - 4465 | | Authorized officer Georgopoulos, N Telephone No. +49 89 2399 2634 | |



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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL00/00059

I. Basis of this report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-21 as originally filed

Claims, No.:

1-15 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00059

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | |
|-------------------------------|------------------|
| Novelty (N) | Yes: Claims 1-15 |
| | No: Claims |
| Inventive step (IS) | Yes: Claims 1-15 |
| | No: Claims |
| Industrial applicability (IA) | Yes: Claims 1-15 |
| | No: Claims |

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

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- 1 Reference is made to the following documents:

D1: US-A-5 576 043

D2: EP-A-0 768 042

D3: EP-A-0 884 003

D4: US-A-4 504 509

D5: EP-A-0 898 902

- 2 The present invention fulfils the requirements of Art.33 (2) PCT, as the subject-matter of independent claims 1 (composition), 9 (use), 12 (method), 14 (foodstuff) and 15 (confectionery) is new.

- 2.1 None of the documents D1 to D5 brings to light depolymerised starch as claimed in present claim 1.

- 2.2 D1 discloses a shortening substitute comprising:

i/ 1 to 10% by weight pregelatinized, unmodified starch selected from the group consisting of a pregelatinized high amylose starch; and

ii/ 5 to 15% by weight pregelatinized, modified, high amylopectin starch, said modified starch being selected from the group consisting of pregelatinized, crosslinked, hydroxypropylated starch and pregelatinized, crosslinked, esterified starch (see claims 1 and 2 as well as examples 1 to 14 of D1).

D2 discloses a mayonnaise-like product comprising carrageenan and starch, characterised in that the starch is selected from the group consisting of hydroxypropyl distarch phosphate and acetylated distarch adipate, phosphorylated distarch phosphate and acetylated distarch phosphate (see claims 1, 2 and 7 of D2).

D3 discloses a UHT lactic cream containing modified starch, xanthan and maltodextrines (see example 1 and claim 1 of D3).

D4 brings to light an aseptically processed liquid batter comprising starch dextrin and starch, wherein said starch is highly crosslinked to a level enabling the starch

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL00/00059

granules to remain in the substantially ungelatinized state through aseptic processing (see example I and claims 1 and 2 of D4).

Finally, D5 discloses improved aqueous starch enrobing slurries comprising ungelatinized starch and not less than 50% rice flour, wherein said ungelatinized starch may be a slightly modified starch having a crosslinking level of less than 400 ppm based on crosslinking with POCl_3 (see page 3, lines 3 to 15 of D5).

2.3 Moreover, the subject-matter of present claims 9, 12, 14 and 15 is also new vis-à-vis D1 to D5, because the above-mentioned depolymerised starch is a technical feature of said claims.

3 The subject-matter of present claims 1-8 involves an inventive step (Art.33 (3) PCT), for the following reasons:

3.1 D1 is considered to be the closest prior art document. The problem to be solved by the present invention may, therefore, be seen in as how to provide a starch composition demonstrating improved properties to those of gelatine, most notably improved:

i/ clarity; and

ii/ elasticity of the foodstuff, when said composition is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). The difference between present invention's starch composition and that of D1 is that the former comprises depolymerised starch (see points 2.1 and 2.2 above). Both said depolymerised starch and the cross-linked starch of present invention's composition bring about the two above-mentioned technical advantages (see page 7, line 29 to page 8, line 9 of the present invention). There are no indications in any of the documents D2 to D5 that would prompt the person skilled in the art to start from the composition of D1, modify it and arrive at the alleged invention, as none of said documents discloses depolymerised starch either (see points 2.1 and 2.2 above). Thus, the subject-matter of claims 1-8 would not be obvious to the person skilled in the art having regard to D1, D2, D3, D4 and D5.

4 The subject-matter of claims 9-11 involves an inventive step (Art.33 (3) PCT), the reasons being as follows:

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- 4.1 D1 is considered to be the closest prior art document. The problem to be solved by the present invention may, therefore, be seen in as how to provide the use of a starch composition in the preparation of a foodstuff, wherein said composition demonstrates improved properties to those of gelatine, most notably improved:
- i/ clarity; and
 - ii/ elasticity of the foodstuff, when it is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). As present invention's composition would not be obvious to the person skilled in the art vis-à-vis D1 to D5 (see point 3.1 above), its use for the production of a foodstuff would not be either.
- 5 The subject-matter of claims 12-13 involves an inventive step (Art.33 (3) PCT). The problem to be solved by the present invention over D1 (closest prior art document) may be regarded as how to provide a method for the preparation of a thickened foodstuff comprising mixing a starch composition with water, wherein said composition demonstrates improved properties to those of gelatine, most notably improved:
- i/ clarity; and
 - ii/ elasticity of the foodstuff, when it is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). As present invention's composition would not be obvious to the person skilled in the art having regard D1 to D5 (see point 3.1 above), said method would not be either.
- 6 The subject-matter of claims 14 and 15 involves an inventive step too (Art.33 (3) PCT). The problem to be solved by the present invention over D1 (closest prior art document) may be regarded as to provide a foodstuff or a confectionery (both comprising a starch composition), wherein said composition demonstrates improved properties to those of gelatine, most notably improved:
- i/ clarity; and
 - ii/ elasticity of the foodstuff, when it is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). As present invention's composition would not be obvious to the person skilled in the art having regard D1 to D5 (see point 3.1 above), said foodstuff and confectionery would not be either.

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL00/00059

- 7 The subject-matter of claims 1 to 15 is susceptible of industrial application in the field of food industry (Art.33 (4) PCT).

Item VII

- 8 The following "obvious errors" (Rule 91 (1) (b) PCT) have not been corrected:
- i/ on page 5, line 4 and page 15, line 3, " POCl_3 " instead of " POCl_3 ";
 - ii/ on page 6, line 7, "hydrolysed" instead of "hydrolysis";
 - iii/ on page 14, line 15, "Therefore" instead of "Therefor";
 - iv/ on page 15, line 35, " H_2O_2 " instead of " H_2O_2 ";
 - v/ on page 19, line 26, " 130°C " instead of " 1300C "; and
 - vi/ on page 21, line 15, "texture. " instead of "texture".

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PATENT COOPERATION TREATY

PCT/NL00/00059

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From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

| | |
|------------------|---|
| Kopie in/naar | TERMINAL |
| | 15 AUG 2000 |
| | Date of mailing (day/month/year) 03 August 2000 (03.08.00) |
| | Applicant's or agent's file reference MAP P48544PC00 |

| |
|--|
| To: OTTEVANGERS, S., U. Vereenigde Nieuwe Parklaan 97 NL-2587 BN The Hague PAYS-BAS <i>NRF₂ 29-7-2001 Gum</i> <i>Sl. rapp ? ok</i> |
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IMPORTANT NOTICE

| | | |
|--|--|--|
| International application No. PCT/NL00/00059 | International filing date (day/month/year) 28 January 2000 (28.01.00) | Priority date (day/month/year) 29 January 1999 (29.01.99) |
| Applicant COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL EN DERIVATEN AVEBE B.A. et al | | |

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
AU,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,
GE,GH,GM,HR,HU,ID,IL,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,NO,
NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW
The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
03 August 2000 (03.08.00) under No. WO 00/44241

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

| | |
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| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35 | Authorized officer J. Zahra Telephone No. (41-22) 338.83.38 |
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
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| (51) International Patent Classification ⁷ : A23L 1/0522, 1/09 | A1 | (11) International Publication Number: WO 00/44241 (43) International Publication Date: 3 August 2000 (03.08.00) |
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COMPOSITION BASED ON CROSS-LINKED STARCH AND DEPOLYMERIZED STARCH SUITABLE AS GELATINE REPLACEMENT

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The invention relates to hydrocolloids that are used as thickening, binding, gelling or stabilising agents in the food industry.

In the food industry hydrocolloids are in general used to thicken (gel, bind, stabilise) water-based foodstuffs. Gelatine is a popular hydrocolloid, which, contrary to other hydrocolloids which are mainly of a polysaccharide nature, is a protein. Gelatine is derived from animal slaughter offal, such as skins and bones, by hydrolysis of insoluble collagen into soluble gelatine. Collagen is the major structural component of white tissue fibres and present in all tissues and organs of animals where it constitutes almost 30% of total protein content.

Gelatine is used in a great number of food applications, where it is desired because it has a number of characteristics that are superior over other hydrocolloids used in the food industry. It is used for example as a thickening or gelling agent in jellied products such as confectionery and aspic type of foods; as a stabiliser and thickener in ice cream and icings, as emulsifier and thickener in dressings, desserts and sauces, as thickener in syrups and soups, as binder or thickener in general and as fining agent. For example, gelatine is used in gum and jelly products, such as wine gums, as gelling agent to give the end product an elastic, gummy structure. In particular, gelatine is superior over other thickening (gelling and binding) agents for the clarity and elasticity it renders to the food product.

The use of gelatine (or hydrolysed collagen) in the food industry, however, has recently been criticised because of its animal origin. Traditionally, gelatine containing foodstuff has been avoided by vegetarian

consumers and by consumers whose religion teaches to avoid animal derived products like gelatine. These traditional gelatine avoiding consumers were in general satisfied with buying products that contained less
5 superior binding agents to accommodate their vegetarian and/or religious preferences. More recently, however, the general consumer, albeit not bound by vegetarian or religious preferences, is also shifting to a preference for foodstuff wherein gelatine is replaced by another
10 agent. Said shift in the preference of the general public is mainly understood to have been initiated by the recent occurrence of prion diseases such as seen with mad cow disease, and by concern that these prion diseases may infect humans when proteinaceous food of animal origin is
15 eaten.

The prion diseases bovine spongiform encephalopathy (BSE) and scrapie of cattle and sheep, respectively, are fatal neurodegenerative diseases caused by prion proteins and are characterised by a long incubation period. In
20 humans Creutzfeldt-Jakob disease (CJD), Gerstmann-Sträussler-Scheinker syndrome (GSS) and fatal familial insomnia belong to this category of transmissible spongiform encephalopathies (TSEs). Although scrapie, the prototype of the family of TSEs, in sheep and goats has
25 been known for over 200 years and has been diagnosed world-wide, it is only since 1986 that BSE has been described in cattle in the UK. By January 1998, there had been 170,259 confirmed cases of BSE in Great Britain and there may exist a great number of cases of not yet overt
30 cases of BSE. BSE apparently emerged because scrapie contaminated sheep offal, via meat and bone meal had been included in cattle feeding-stuff, and newly infected cattle material was then recycled and eaten by
susceptible cattle. Brain homogenates from cows with BSE
35 produce a characteristic pattern of brain lesions in mice. This is identical to the pattern elicited by brain

tissue from individuals who recently have died from new-variant Creutzfeldt-Jakob disease. Up to now, this variant has caused the death of 35 young Britons and one Frenchman.

5 There is also concern that the BSE strain that seems to be transmissible to humans may have infected sheep, where it could produce a disease hardly distinguishable from scrapie. Sheep BSE may be a threat to human health, although scrapie by itself seems not to transmit to
10 humans. Indeed, BSE agent has been transmitted experimentally to sheep by the oral route and thus could have the potential to infect sheep under field conditions.

 Thus far, the only known cause of prion disease is
15 an abnormal form of the normal prion protein called aberrant prion protein. Said aberrant prion protein is mainly characterised by its resistance to proteolytic hydrolysis, it is typically quite resistant against treatment with high or low pH, and generally only loses
20 its infectivity after prolonged treatment under high temperature.

 Although most governments in Western society have taken strict measurements to alleviate public concerns related to mad cow disease, for example by strictly
25 banning the use of animal products derived from animals with prion disease in the food industry, public concerns related to using the protein derived gelatine still exist, and seem to be growing. Consequently, among the general public lives a growing desire to consume non-
30 gelatine derived foodstuff, that, however, has similar or comparable superior characteristics as the traditionally gelatine comprising foodstuffs have.

 It is an object of the present invention to provide a non-protein hydrocolloid that has suitable
35 characteristics to serve as gelatine replacement in

foodstuff of varied nature or that can be used to prepare new types of foodstuff.

The invention provides a starch composition,
5 comprising a first fraction comprising cross-linked starch and at least a second fraction comprising depolymerised starch. Said composition is suitable for example to serve as gelatine replacement in foodstuff of varied nature, and is preferably suitable for use in
10 foodstuff such as confectionery. Starches suitable for use in a composition according to the invention are for example chosen from maize, wheat, barley, rice, triticale, rice, millet, tapioca, arrow root, banana, potato, sweet potato starches or from high amylose
15 starches like amylo maize, wrinkled pea starch, mung bean starch or from amylopectin rich starches like waxy maize, waxy barley, waxy wheat, waxy rice, amylopectin potato, amylopectin tapioca, amylopectin sweet potato or amylopectin banana starch. Amylopectin starches may be
20 derived from plants that selectively produce amylopectin such as waxy cereals or amylose-free potato mutants and/or genetically modified plant varieties such as potatoes modified to selectively produce amylopectine. Cross-linked starch in general is a modified starch in
25 which cross-links between starch macromolecules have been formed by means of bifunctional or polyfunctional chemical reagents, and results in the formation of large complexes of starch molecules with high molecular weight. Cross-links can for example be formed between amylose
30 molecules or between amylopectine molecules, or between amylose and amylopectine molecules in the starch. Although not preferred from the viewpoint of ease of production, a first fraction according to the invention can of course also be partly depolymerised, or be
35 modified in any other way, and a second fraction according to the invention can also be partly cross-linked, or be modified in any other way, if so desired.

Cross-linking starch in itself is a method known in the art and various agents are known. Examples are: epichlorohydrin, sodium trimetaphosphate, phosphorous oxychloride (POCl_3), adipic anhydride, or other reagents with two or more halogen, halohydrin or epoxide groups or combinations which all can be used as cross-linking agents. Preferred are distarch phosphates and distarch adipates. A cross-linked or cross-bonded starch may for example be cross-bonded by 0.003 to 0.024% of adipic anhydride, preferably by 0.01 to 0.03%. Prior to cross-bonding by adipic anhydride the starch may be treated with hydrogen peroxide and/or peracetic acid. Preferably with a quantity which corresponds to 0.001% to 0.045% of active oxygen, most preferably to 0.005 to 0.045%. A distarch phosphate may for example be cross-bonded by sodium trimetaphosphate up to such a degree that the residual phosphate is no more than 0.14% for a potato starch or 0.04% for other starches. Preferably the starch is cross-bonded with 0.01% to 0.25%, most preferably with 0.025 to 0.15% of sodium trimetaphosphate, under conditions known to the artisan. Of course it is always possible for the artisan to find conditions in which the reactants react with a very low yield, outside of the preferred conditions resulting in a starch with desired properties. A distarch phosphate may as well be cross-bonded with phosphorous oxychloride up to such a degree that the residual phosphate is not more than 0.14% for a potato starch or 0.4% for other starches. Preferably the starch is cross-bonded with 0.00010 % to 0.01% of phosphorous oxychloride, under conditions known to the artisan. Of course it is always possible for the artisan to find conditions in which the reactants react with a very low yield, outside of the preferred conditions resulting in a starch with the desired properties.

Depolymerised starch is in general obtained by a reduction in the degree of polymerisation of the starch chains by physical, chemical or enzymatic action, and results in general in a reduction of the size (molecular

weight) of the starch molecules. Depolymerisation by acid hydrolysis of starch can be accomplished in many ways known to the artesian. Preferred enzymatic hydrolysis, acid catalysed hydrolysis using organic or mineral acid and dry roasting of starches under acidic conditions (dextrination). In an embodiment of the invention the starch is hydrolysis in a slurry process using hydrochloric or sulphuric acid. During hydrolysis with acid the molecular weight of the starch by hydrolytic cleavage of the acetal function of the starch.

Depolymerisation by oxidation of starch can also be accomplished an large number of ways. Known oxidation agents are sodium hypochlorite, calcium hypochlorite, sodium and potassium permanganate and hydrogen peroxide. Preferred is the hypochlorite oxidation of starch which is still one of the most useful reactions for the derivatisation of starches. Oxidised starches are applicable in a wide range of applications such as paper manufacture, adhesives, textile industry and food.

Hypochlorite is a relatively cheap oxidation agent. During oxidation with hypochlorite different oxidation reaction may take place, of which the hydrolysis of the glucosidic bonds is the most important. Together with a decrease in molecular weight of the starch molecule also functional groups such as carbonyl and carboxyl groups are introduced. The instability of the glucosidic bonds is influenced by the presence of carbonyl or carboxyl groups. The course of an oxidation reaction is primarily controlled by the amount of hypochlorite, the pH, the temperature and the presence of a catalyst. An overview of the most important reaction parameters is depicted in article by J. Potze and P. Hiemstra in Starch; volume 15, page 217-225 (1963). The decrease in molecular weight, and the amount of functional groups is direct proportional to the amount of hypochloride. The oxidation rate is very sensitive for the pH during oxidation. The

highest reaction rates are obtained at neutral pH (pH about 7), the reaction rate decreases with increasing pH. The carbonyl content of oxidised starches is also controlled by the pH. At neutral pH the highest carbonyl contents are obtained. Due to this high amount of carbonyl groups, also a high amount of hydrolyses of the glucosidic bonds is observed at neutral pH, resulting in a decrease in viscosity of the resulting oxidised starch derivative. Increasing the oxidation pH results in a steady decrease in both carbonyl content and hydrolysis of the glucosidic bonds. Unfortunately, a high amount of carbonyl groups leads to viscosity instability of the oxidised starch. The introduction of carboxyl groups give rise to an increase in viscosity stability of the oxidised starch. Here too the amount of carboxyl groups is controlled by the pH, with a maximum at pH 9. Hypochlorite oxidations are mainly performed in slurry processes. The degradation of starch can be monitored by measuring the intrinsic viscosity. The intrinsic viscosity of depolymerised granular products lies between 0.2 and 2.5 dL/g, preferably between 0.3 and 1.5, mostly preferred between 0.4 and 1.2.

Surprisingly, by combining said fractions, each having distinct characteristics, a starch composition is obtained that demonstrates characteristics comparable to characteristics of gelatine, or even improving those of gelatine, most notably those relating to clarity and elasticity of the foodstuff when said composition is used as binding, thickening or gelling agent. Combining said two fractions according to the invention imparts said desired characteristics to the starch composition, making it suitable to use the composition as provided by the invention in the food industry to partly or even fully replace gelatine and to prepare new types of foodstuff. Said composition comprising said two fractions can for example be obtained by mixing separate starch fractions,

a cross-linked fraction and a depolymerised fraction, in the desired ratio to obtain a starch composition as provided by the invention, however, it is also possible to obtain said composition by partial cross-linking and
5 partial depolymerisation of a starch. However, a mixture of at least two fractions is preferred in the light of obtaining a starch composition according to the invention that is adjusted to for example the level of elasticity and/or clarity required of the foodstuff.

10 By virtue of the diverse fractions, said starch composition demonstrates characteristics that are close to or even improved over those of gelatine. The ratio at which the fractions shall be used are easily determined by mixing and testing the thus obtained compositions for
15 desired properties. Suitable ratios of first fraction to second fraction (weight%:weight%) vary for example from 5:95 to 95:5, preferably from 10:90 to 90:10, more preferably from 25:75 to 75:25. For example, soft food products, such as soft sugar confectionery in which
20 gelatine is traditionally used most, desire most elasticity, and by adjusting the ratio of the two fractions in the starch composition as provided by the invention, the desired clarity and/or elasticity can be obtained. Also, in hard confectionery products, where
25 traditionally hydrolysed collagen is used in mixtures to replace gums, such as gum arabic, clarity and/or elasticity are now obtained using a starch composition according to the invention. In general when more elasticity is required, one increases the cross-linked
30 fraction, and when more gelling and/or clarity is desired one increases the depolymerised fraction.

In a preferred embodiment, the invention provides a starch composition comprising a first fraction comprising cross-linked starch and at least a second fraction
35 comprising depolymerised starch wherein said first fraction is cross-linked by using sodium trimetaphosphate,

phosphorus oxytrichloride or adipic anhydride, using for example a method known in the art. These cross-linking agents are most suitable for use in the food industry.

Preferred are cross-linked starch acetates having an acetyl content which corresponds to a DS or degree of substitution of 0.001 to 0.2, preferably from 0.03 to 0.092, most preferably from 0.05 to 0.092. The term DS used herein indicates the average number of sites per anhydroglucose unit of the starch molecule in which there are substituent groups.

Even more preferred are cross-linked hydroxypropylated starches having a hydroxypropyl content which corresponds to a DS of 0.001 to 0.3, preferably, 0.03 to 0.21, most preferably 0.06 to 0.21.

In a further preferred embodiment the invention provides a starch composition according to the invention wherein said first fraction is also stabilised. Stabilisation in general is done by methods known in the art, such as by treatment with acetic anhydride or vinyl acetate, or comparable agents, but for the purpose of gelatine replacement a preferred embodiment is a composition according to the invention wherein said first fraction is stabilised by hydroxyalkylation, for example by hydroxypropylation. Stabilisation by hydroxyalkylation of starch is for example obtained with reagents containing a halohydrin, or an epoxide group as reactive site. The addition of hydroxypropyl groups is generally performed in aqueous suspensions of starch using propylene oxide, under alkaline conditions. Cross-bonding and/or stabilising reagents are reacted with starch under alkaline conditions. Suitable alkali materials are: sodium hydroxide, potassium hydroxide, ammonium hydroxide, magnesium hydroxide, sodium carbonate and trisodium phosphate. Preferred are the alkali metal hydroxides and carbonates, most preferred are sodium hydroxide and sodium carbonate. Sometimes salts are added as to prevent swelling under alkaline reaction conditions. Preferred are sodium chloride and sodium

sulphate.

In a further embodiment, the invention provides a starch composition comprising a first fraction comprising cross-linked starch and at least a second fraction comprising depolymerised starch wherein said depolymerisation is for example achieved by acid or enzymatic hydrolysis. Preferred for the purpose of gelatine replacement, however, is a composition according to the invention wherein said second fraction is obtained by oxidation of starch, such as by treatment with sodium hypochlorite or hydrogen peroxide.

In a further preferred embodiment the invention provides a starch composition according to the invention wherein said second fraction is also stabilised. Stabilisation in general is done by methods known in the art, such as by hydroxyalkylation or by acetylation with acetic anhydride, vinyl acetate or comparable agents. For the purpose of gelatine replacement a preferred embodiment is a composition according to the invention wherein said second fraction is stabilised by acetylation. Stabilisation by acetylation is performed using acetic anhydride or vinyl acetate. Other stabilisation reagents are for example succinic anhydride, 1-octenyl succinic anhydride, sodium tripolyphosphate, potassium orthophosphate, sodium orthophosphate or orthophosphoric acid. In yet another embodiment, said second fraction is also cross-linked, for example by a suitable method as listed above, to provide even more elasticity (chewiness).

The invention also provides use of a starch composition according to the invention in the preparation of a foodstuff, preferably partly or fully replacing gelatine in said foodstuff. By using a composition according to the invention, it is possible to replace gelatine for more than 50%, up to 80% or even 100%, depending on the requirements of the customer. It is thus now possible to reduce gelatine content and select and

use minimal quantities of those gelatine batches that are absolutely prion protein free, or to fully replace animal derived thickeners, such as hydrolysed collagen, or gelatine, that may be derived from slaughter offal
5 comprising aberrant prion protein. In a preferred embodiment, said foodstuff comprises confectionery, for example sugar confectionery such as hard or soft sugar confectionery, lozenges or dragees, or confectionery for diabetics wherein the sugar is replaced by artificial
10 sweeteners.

The invention furthermore provides a method for preparing a thickened (thickening herein also called gelling, stabilising or binding) foodstuff comprising
15 mixing a starch composition according to the invention with a water-based liquid. Such a water-based liquid can for example be water, milk or another dairy product, a stock or bouillon, a sugar solution, a beverage or another water-based liquid food component known in the art. Of course, said method allows for the additional use
20 of other ingredients, of which many are known in the art. Traditionally, gelatine was a first choice in thickening such liquids, however, due to consumer preference, a method to prepare non-gelatine foodstuffs is desired.

Furthermore, the invention provides foodstuff
25 comprising a starch composition comprising a first fraction comprising cross-linked starch and at least a second fraction comprising depolymerised starch. Such foodstuff can for example be characterised by a clarity and/or elasticity that in general lives up to consumers
30 expectations relating to gelatine comprising foodstuffs. In a preferred embodiment the invention comprises confectionery, as further exemplified in the detailed description herein without limiting the invention.

Detailed description

General overview of confectionery production

5

Sugar-based products, or sugar confectionery, can be divided into the following groups.

1. Hard sugar confectionery (fruit drops, clear mints,
10 barley sugars, and bonbons)
2. Soft sugar confectionery (gums, pastilles, jellies,
 chewing gums, gelées, liquorice)
3. Lozenges (sheeted/pressed confectionery)
4. Dragees (coated confectionery).

15

In sugar confectionery starch products, natural gums and proteins are traditionally used as binding and/or gelling agents. There are two main types of soft sugar: gummy products like fruit gums, liquorice gums, pastilles, etc.
20 and elastic products like wine gums, jellies, etc. A binding and/or gelling agent itself has specific properties, which influences the properties of the final product. For soft sugar confectionery applications gelatine is traditionally used as gelling agent, as it
25 imparts a desired elasticity to the end product. In soft sugar confectionery thin boiling starches are commonly used to replace gelatine in part, however replacement of gelatine with thin boiling starches leaves the customer with products having a low acceptance as they have little
30 elasticity.

The application of gelatine and mixtures of gelatine and thin boiling starches in soft confectionery is a well-known process. For instance in "Sugar Confectionery Manufacture" edited by E.B. Jackson, Blackie and Son,
35 London 1990 an overview of different process equipment and product recipes are given. Gums, pastilles and

jellies can be processed using a variety of techniques, batch cooking, direct cooking (jet cooker), indirect cooking or extrusion cooking. Batch process proceeds through atmospheric cooking in open pans. Colouring, 5 flavouring and moulding and drying in starch moulds follows cooking. Direct cooking comprises two parts: cooking and a vacuum cooling part. The confectionery mass is pumped into the continuous (jet)cooker where it is heated with steam. The pressure of the steam 10 determines the cooking temperature. The slurry is then pumped into the vacuum cooler, where it is cooled and all air removed. When the required concentration is reached, colours and flavouring can be added. The slurry can then be formed.

15 The present invention among others relates to the partial or full replacement of gelatine in confectionery. This can be for example be achieved by a using a starch composition comprising a combination of a thin boiling starch and cross-linked and stabilised starch. In one 20 embodiment of the present invention the thin boiling starch is prepared by oxidation or acid degradation of starch. The starch may be oxidised by sodium hypochlorite or by hydrogen peroxide. The acid degradation may be performed with hydrochloric acid or sulphuric acid in 25 slurry process.

Alternatively, the acid degradation can be achieved through a dextrination process using hydrogen chloride or sulphuric acid applying heat. The cross-bonding can be performed with sodium trimetaphosphate, phosphorus 30 oxytrichloride or adipic anhydride using procedures known to the artesian. The stabilisation can be performed with propylene oxide, acetic anhydride or vinyl acetate. A thin boiling starch is for example stabilised and oxidised or stabilised acid degraded.

35

Analytical procedures

Sensory evaluation

- 5 The confectionery was tested by a trained panel for a number of sensor features. The products were evaluated on a sensoric scale from 1 to 5, and a general acceptance scale from 1 to 10.
- 10 Testing the end products for the presence of cross-bonded starch derivatives

In order to determine the cross-linked starch in confectionery a sedimentation test was carried out.

- 15 Therefor 20 gram wine gum was dissolved in a potassium dihydrogen phosphate/ sodium hydroxide buffer at pH at 90 °C to give a solution of approx. 20%. The solution was cooled to room temperature and the amount of dry substance was measured with a refractometer. Then this solution was
- 20 diluted to a 5 % solution with demineralised water. 100 ml solution was allowed to stand for 24 hours in a measuring cylinder. Afterwards the amount of sedimentation was estimated. The cross-linked starch could be identified under a microscope also.

25

Intrinsic viscosity (IV)

- The intrinsic viscosity is determined in a known manner with a Ubbelohde viscosity meter with 1 M sodium
- 30 hydroxide as solvent and expressed in g/dl.

Example 1

The preparation of cross-linked hydroxypropylated starch

35

A 39 % starch slurry is prepared. To this slurry sodium

5 sulphate (100 g/kg) and sodium hydroxide (7.5 g/kg starch) as 4.4 % solution are added. The temperature was raised to 35 °C and POCl_3 is added (15 to 200 $\mu\text{L/kg}$ depending on the degree of cross-linking). Next
10 propylene oxide ($\text{DS}_{\text{max}} = 0.225$) is introduced and the reaction was allowed to proceed 20-24 hours. The slurry was neutralised with sulphuric acid to pH 5-6 and washed and dried using conventional means known to the art. The starch used are potato starch and tapioca starch.

Example 2

The preparation of cross-linked acetylated starch

15 A 39 % starch slurry is prepared of 1 kg of potato starch. To this slurry 25 g of sodium chloride and sodium hydroxide (7.5 g/kg starch) as 4.4 % solution are added. The temperature was raised to 35 °C and sodium
20 trimetaphosphate (400 or 600 mg depending on the degree of cross-linking) is added. The reaction is allowed to proceed for 6 hours. The slurry was neutralised with sulphuric acid to pH 8.5 and 61 g of acetic acid is added drop wise. After the decline of reaction the suspension
25 is neutralised with sulphuric acid to pH 5-6 and washed and dried using conventional means known to the art.

Example 3

The preparation of adipylated, acetylated starch

30 The adipate/acetate of amylopectin potato starch was prepared using a 1:20 mixture. 810 gram dry starch was suspended in water to 39 % suspension. The pH was adjusted to 8.5 with a 4.4 % (w/w) sodium hydroxide
35 solution and 1.3 ml of 30 % of H_2O_2 solution were added. Then 6 g of 1:20 adipic anhydride reagent was added drop

wise keeping the pH at 8.5 with a 4.4 % (w/w) sodium hydroxide solution. Afterwards 41 grams of acetic anhydride was added drop wise to a pH 8.5. The acetic anhydride reaction was performed in approx. 1.5 hours.

5 After the acetic anhydride dosage the suspension was stirred for 10 minutes at pH 8.5. Then the suspension was neutralised with sulphuric acid to pH 5.5 and the final product was dewatered, washed and dried using methods known to the art.

10

Example 4

The preparation of acid-degraded starch

15 A 39 % starch slurry is prepared of 1 kg of potato starch and water. To this slurry 80 ml of 10 N sulphuric acid are added. The temperature was raised to 45 °C. The reaction is allowed to proceed 17 hours. The slurry is neutralised with sodium hydroxide to pH 5-6 and washed

20 and dried using conventional means known to the art.

Example 5

The preparation of oxidised starch

25

Starch was oxidised in aqueous suspension with sodium hypochlorite using sodium hydroxide as a catalyst. Thus 810 gram dry starch was suspended in water to 39-% suspension. The temperature of the suspension was

30 adjusted at 35 °C. Sodium hypochlorite was added, amounts corresponding with 10 grams of active chlorine and at the same time sodium hydroxide was added, as a 4.4 % (w/w) solution, adjusting the pH to a value of 11. During the reaction the pH is kept at 11. When there was

35 no active chlorine detectable the suspension was bleached with 5 ml sodium hypochlorite and after 1 minute the

excess of chlorine was removed using sodium hydrogen sulphite.

Afterwards the suspension was neutralised with sulphuric acid to pH 5.5 and the final product was dewatered, washed and dried using methods known to the art.

Example 6

The preparation of oxidised acetylated starch

Potato starch was oxidised in aqueous suspension with sodium hypochlorite using sodium hydroxide as a catalyst. Thus 810 gram dry starch was suspended in water to 39 % suspension. The temperature of the suspension was adjusted at 35 °C. Sodium hypochlorite was added, amounts corresponding with 10 grams of active chlorine and at the same time sodium hydroxide was added, as a 4.4 % (w/w) solution, adjusting the pH to a value of 11. During the reaction the pH is kept at 11. When there was no active chlorine detectable the suspension was bleached with 5 ml sodium hypochlorite and after 1 minute the excess of chlorine was removed using sodium hydrogen sulphite. Afterwards the suspension was neutralised with sulphuric acid to pH 8.5. The temperature was adjusted to 25 °C and the suspension was acetylated using 36 g of acetic anhydride at a constant pH value of 8.5. The acetic anhydride reaction was performed in approx. 1.5 hours. After the acetic anhydride dosage the suspension was stirred for 10 minutes at pH 8.5. Then the suspension was neutralised with sulphuric acid to pH 5.5 and the final product was dewatered, washed and dried using methods known to the art. According to the examples 1-6 the following starches were prepared.

Table 1.

| product | starch | modification | amount of cross-linker |
|---------|-----------------------|--------------------------------------|------------------------|
| 1 | potato | oxidation | |
| 2 | tapioca | hydroxypropylation/ cross-linking | 85 μ L/kg |
| 3 | potato | hydroxypropylation/ cross-linking | 15 μ L/kg |
| 4 | potato | hydroxypropylation/ cross-linking | 40 μ L/kg |
| 5 | potato | acetylation/ cross-linking | 100 μ L/kg |
| 6 | potato | acetylation/ cross-linking | 400 mg/kg |
| 7 | potato | acetylation/ cross-linking | 600 mg/kg |
| 8 | amylopectin potato | adipylation/ acetylation | 6 g/kg |
| 9 | potato | acid degradation | |
| 10 | potato | oxidation/ acetylation | |

Example 7

Preparation of wine gum using batch process

5

- A starch suspension is prepared using a starch : water ratio of 1 : 1.5 Into a batch-cooker (open pan) hot water is filled. Glucose-syrup (DE 42; Dormamix 42/82, Pfeiffer & Langen) is added and stirring is started. The
- 10 cooker is heated and sugar is added while stirring. The heating continued until the mixture starts to boil. At this moment the starch suspension is added slowly, while stirring. Boiling is maintained until the desired dry solid is reached (74 -76 %)
- 15 The mixture is cooled to 80 °C and colour, flavour and citric acid are added. The cooked solution is moulded into shapes in moulding powder. The resulting are dried for 24 hours at 50 °C.

20 Example 8

Preparation of wine gum using direct cooking

- A premix is made of a recipe containing sugar/glucose
- 25 syrup (DE42; Dormamix 42/82, Pfeiffer & Langen), starches and water. This premix is cooked at 1300C in a continuous cooker system from Vomatec. The cooked solution is cooled by applying vacuum. Colour, flavour and citric acid are added to the cooled solution. This
- 30 solution is moulded into shapes in moulding powder. The moulded products are dried and subsequently evaluated.

According to example 8 the following mixtures were prepared and moulded into shapes.

35

Table 2.

| Exp. nr | A | B | C | D | E | F | G | H | I | J | K | L |
|---------------|----|----|----|----|----|----|----|----|----|----|----|----|
| Starch comp. | | | | | | | | | | | | |
| 1 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | | 8 | | 12 | |
| 2 | 3 | | | | | | | | | | | |
| 3 | | 3 | | | | | | 3 | | | | 3 |
| 4 | | | 3 | | | | | | | | | |
| 5 | | | | 3 | | | | | | | | |
| 6 | | | | | 3 | | | | | | | |
| 7 | | | | | | 3 | | | | | | |
| 8 | | | | | | | 3 | | | | | |
| 9 | | | | | | | | 9 | | 8 | | |
| gelatine* | | | | | | | | | 4 | | | |
| gelatine* | | | | | | | | | | 4 | | |
| 10 | | | | | | | | | | | | 9 |
| sugar | 34 | 34 | 34 | 34 | 34 | 34 | 34 | 34 | 30 | 30 | 34 | 34 |
| Glucose-syrup | 34 | 34 | 34 | 34 | 34 | 34 | 34 | 34 | 38 | 38 | 34 | 34 |
| water | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |

gelatine 240 bloom

The resulting products were evaluated. The results are
 5 summarised in table 3.

Table 3.

| Exp. | elast. | clarity | general |
|------|--------|---------|---------|
| A | 4 | 3 | 7 |
| B | 4 | 3 | 6 |
| C | 4 | 3 | 7 |
| D | 4 | 2 | 3 |
| E | 3 | 3 | 4 |
| F | 3 | 2 | 3 |
| G | 3 | 3 | 3 |
| H | 3 | 3 | 3 |
| I | 4 | 3 | 7 |
| J | 4 | 3 | 7 |
| K | 1 | 1 | 2 |
| L | 5 | 4 | 8 |

Example 9

5

Preparation of liquorice

| | | |
|----|--|-----|
| | Product 1 | 9% |
| | Product 3 | 3% |
| 10 | Sugar | 28% |
| | Glucose-syrup DE 42 | 32% |
| | Ammonium chloride | 4% |
| | Liquorice powder | 4% |
| | Water | 20% |
| 15 | The resulting liquorice had a gummy, elastic texture | |

CLAIMS

1. A starch composition comprising a first fraction comprising cross-linked starch and at least a second fraction comprising depolymerised starch.
2. A composition according to claim 1 wherein said
5 first fraction comprises starch cross-linked by using sodium trimetaphosphate, phosphorus oxytrichloride or adipic anhydride.
3. A composition according to claim 1 or 2 wherein said first fraction further comprises stabilised starch.
- 10 4. A composition according to claim 3 wherein said first fraction is stabilised by hydroxyalkylation.
5. A composition according to anyone of claims 1 to 4 wherein said second fraction comprises depolymerised starch obtained by oxidation.
- 15 6. A composition according to any one of claims 1 to 5 wherein said second fraction further comprises stabilised starch.
7. A composition according to claim 6 wherein said second fraction is stabilised by acetylation.
- 20 8. A composition according to anyone of claims 1-7 wherein said starch is derived from potato.
9. Use of a starch composition according to anyone of claims 1 to 8 in the preparation of a foodstuff.
10. Use according to claim 9 wherein the use of said
25 composition at least partly replaces the use of gelatine in said foodstuff.
11. Use according to claim 9 or 10 wherein said foodstuff comprises confectionery.
12. A method for preparing a thickened foodstuff
30 comprising mixing a starch composition according to anyone of claims 1 to 8 with a water-based liquid.
13. A method according to claim 12 wherein said foodstuff comprises confectionery.

14. Foodstuff comprising a starch composition according to anyone of claims 1 to 8.

15. Confectionery comprising a starch composition according to anyone of claims 1 to 8.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00059

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A23L1/0522 A23L1/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | US 5 576 043 A (STANKUS CAROL ET AL) 19 November 1996 (1996-11-19) column 3, line 16 -column 4, line 12 column 4, line 59 -column 5, line 58 examples 4,6; table I | 1-4, 9, 12-15 |
| X | EP 0 768 042 A (NESTLE SA) 16 April 1997 (1997-04-16) page 2, line 48 - line 51 examples 1,2 | 1-3, 9, 12, 14 |
| X | EP 0 884 003 A (NESTLE SA) 16 December 1998 (1998-12-16) claim 1; example 1 | 1, 3, 9, 12, 14 |
| | -/- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

14 April 2000

Date of mailing of the international search report

26/04/2000

Name and mailing address of the ISA

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Vuillamy, V

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00059

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | US 4 504 509 A (BELL HARVEY ET AL) 12 March 1985 (1985-03-12) column 3, line 1 -column 4, line 51 table I | 1,2,9, 12,14 |
| X,P | EP 0 898 902 A (PENFORD CORP) 3 March 1999 (1999-03-03) page 4, line 4 --line 49 page 5, paragraph 2 tables 5-11 page 4 | 1-3,6,8, 9,12,14 |

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/NL 00/00059

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| US 5576043 | A | 19-11-1996 | WO 9639863 A | 19-12-1996 |
| EP 0768042 | A | 16-04-1997 | AU 6814896 A | 17-04-1997 |
| | | | CA 2187807 A | 14-04-1997 |
| | | | CZ 9602971 A | 14-05-1997 |
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PATENT COOPERATION TREATY

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PCT 09/889 116

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| | | |
|--|---|--|
| Applicant's or agent's file reference P48544PC00 | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) | |
| International application No. PCT/NL00/00059 | International filing date (day/month/year) 28/01/2000 | Priority date (day/month/year) 29/01/1999 |
| International Patent Classification (IPC) or national classification and IPC A23L1/0522 | | |
| Applicant COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING et al | | |
| <p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p> | | |
| <p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none">I <input checked="" type="checkbox"/> Basis of the reportII <input type="checkbox"/> PriorityIII <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicabilityIV <input type="checkbox"/> Lack of unity of inventionV <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statementVI <input type="checkbox"/> Certain documents citedVII <input checked="" type="checkbox"/> Certain defects in the international applicationVIII <input type="checkbox"/> Certain observations on the international application | | |
| Date of submission of the demand 11/07/2000 | Date of completion of this report 06.02.2001 | |
| Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 | Authorized officer Georgopoulos, N Telephone No. +49 89 2399 2634 | |



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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00059

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-21 as originally filed

Claims, No.:

1-15 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00059

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | | | |
|-------------------------------|------|--------|------|
| Novelty (N) | Yes: | Claims | 1-15 |
| | No: | Claims | |
| Inventive step (IS) | Yes: | Claims | 1-15 |
| | No: | Claims | |
| Industrial applicability (IA) | Yes: | Claims | 1-15 |
| | No: | Claims | |

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL00/00059

It m V

- 1 Reference is made to the following documents:

D1: US-A-5 576 043

D2: EP-A-0 768 042

D3: EP-A-0 884 003

D4: US-A-4 504 509

D5: EP-A-0 898 902

- 2 The present invention fulfils the requirements of Art.33 (2) PCT, as the subject-matter of independent claims 1 (composition), 9 (use), 12 (method), 14 (foodstuff) and 15 (confectionery) is new.

- 2.1 None of the documents D1 to D5 brings to light depolymerised starch as claimed in present claim 1.

- 2.2 D1 discloses a shortening substitute comprising:
i/ 1 to 10% by weight pregelatinized, unmodified starch selected from the group consisting of a pregelatinized high amylose starch; and
ii/ 5 to 15% by weight pregelatinized, modified, high amylopectin starch, said modified starch being selected from the group consisting of pregelatinized, crosslinked, hydroxypropylated starch and pregelatinized, crosslinked, esterified starch (see claims 1 and 2 as well as examples 1 to 14 of D1).

D2 discloses a mayonnaise-like product comprising carrageenan and starch, characterised in that the starch is selected from the group consisting of hydroxypropyl distarch phosphate and acetylated distarch adipate, phosphorylated distarch phosphate and acetylated distarch phosphate (see claims 1, 2 and 7 of D2).

D3 discloses a UHT lactic cream containing modified starch, xanthan and maltodextrines (see example 1 and claim 1 of D3).

D4 brings to light an aseptically processed liquid batter comprising starch dextrin and starch, wherein said starch is highly crosslinked to a level enabling the starch

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granules to remain in the substantially ungelatinized state through aseptic processing (see example I and claims 1 and 2 of D4).

Finally, D5 discloses improved aqueous starch enrobing slurries comprising ungelatinized starch and not less than 50% rice flour, wherein said ungelatinized starch may be a slightly modified starch having a crosslinking level of less than 400 ppm based on crosslinking with POCl_3 (see page 3, lines 3 to 15 of D5).

2.3 Moreover, the subject-matter of present claims 9, 12, 14 and 15 is also new vis-à-vis D1 to D5, because the above-mentioned depolymerised starch is a technical feature of said claims.

3 The subject-matter of present claims 1-8 involves an inventive step (Art.33 (3) PCT), for the following reasons:

3.1 D1 is considered to be the closest prior art document. The problem to be solved by the present invention may, therefore, be seen in as how to provide a starch composition demonstrating improved properties to those of gelatine, most notably improved:

i/ clarity; and

ii/ elasticity of the foodstuff, when said composition is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). The difference between present invention's starch composition and that of D1 is that the former comprises depolymerised starch (see points 2.1 and 2.2 above). Both said depolymerised starch and the cross-linked starch of present invention's composition bring about the two above-mentioned technical advantages (see page 7, line 29 to page 8, line 9 of the present invention). There are no indications in any of the documents D2 to D5 that would prompt the person skilled in the art to start from the composition of D1, modify it and arrive at the alleged invention, as none of said documents discloses depolymerised starch either (see points 2.1 and 2.2 above). Thus, the subject-matter of claims 1-8 would not be obvious to the person skilled in the art having regard to D1, D2, D3, D4 and D5.

4 The subject-matter of claims 9-11 involves an inventive step (Art.33 (3) PCT), the reasons being as follows:

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- 4.1 D1 is considered to be the closest prior art document. The problem to be solved by the present invention may, therefore, be seen in as how to provide the use of a starch composition in the preparation of a foodstuff, wherein said composition demonstrates improved properties to those of gelatine, most notably improved:
- i/ clarity; and
 - ii/ elasticity of the foodstuff, when it is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). As present invention's composition would not be obvious to the person skilled in the art vis-à-vis D1 to D5 (see point 3.1 above), its use for the production of a foodstuff would not be either.
- 5 The subject-matter of claims 12-13 involves an inventive step (Art.33 (3) PCT). The problem to be solved by the present invention over D1 (closest prior art document) may be regarded as how to provide a method for the preparation of a thickened foodstuff comprising mixing a starch composition with water, wherein said composition demonstrates improved properties to those of gelatine, most notably improved:
- i/ clarity; and
 - ii/ elasticity of the foodstuff, when it is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). As present invention's composition would not be obvious to the person skilled in the art having regard D1 to D5 (see point 3.1 above), said method would not be either.
- 6 The subject-matter of claims 14 and 15 involves an inventive step too (Art.33 (3) PCT). The problem to be solved by the present invention over D1 (closest prior art document) may be regarded as to provide a foodstuff or a confectionery (both comprising a starch composition), wherein said composition demonstrates improved properties to those of gelatine, most notably improved:
- i/ clarity; and
 - ii/ elasticity of the foodstuff, when it is used as binding, thickening or gelling agent therein (see page 7, lines 23 to 29 of the present description as well as column 1, lines 58 to 62 of D1). As present invention's composition would not be obvious to the person skilled in the art having regard D1 to D5 (see point 3.1 above), said foodstuff and confectionery would not be either.

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL00/00059

- 7 The subject-matter of claims 1 to 15 is susceptible of industrial application in the field of food industry (Art.33 (4) PCT).

Item VII

- 8 The following "obvious errors" (Rule 91 (1) (b) PCT) have not been corrected:
- i/ on page 5, line 4 and page 15, line 3, " POCl_3 " instead of " POCl_3 ";
 - ii/ on page 6, line 7, "hydrolysed" instead of "hydrolysis";
 - iii/ on page 14, line 15, "Therefore" instead of "Therefor";
 - iv/ on page 15, line 35, " H_2O_2 " instead of " H_2O_2 ";
 - v/ on page 19, line 26, " 130°C " instead of " 1300C "; and
 - vi/ on page 21, line 15, "texture. " instead of "texture".

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